

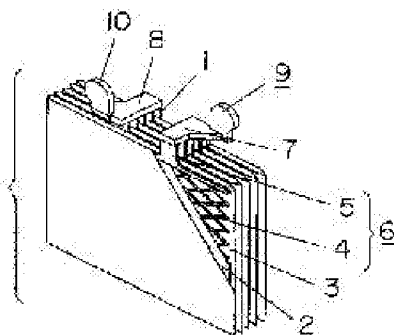
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(21)Application number : 2002-150321 (71)Applicant : MATSUSHITA ELECTRIC IND CO LTD
(22)Date of filing : 24.05.2002 (72)Inventor : YONEMURA KOICHI

(57)Abstract:

SOLUTION: A positive electrode member comprising a positive electrode grid, a positive electrode shelf 8, a positive pole, and positive electrode connecting body 10 is composed of lead or lead alloy substantially including no Sb. A part excluding a negative electrode grid skeleton part out of a negative electrode member comprising a negative electrode grid 6, a negative electrode shelf 7, a negative pole, and a negative electrode connecting body 9 is composed of lead or lead alloy substantially including no Sb. Either one of the negative electrode grid skeleton part or a negative electrode active material includes Sb and the content of the Sb to the amount of the negative active material is 0.001-0.1 mass%.



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CLAIM + DETAILED DESCRIPTION

[Claim(s)]

[Claim 1] It has the positive electrode plate equipped with the positive electrode lattice which consists of a negative electrode plate and a lattice handle part equipped with the negative electrode lattice which consists of a lattice handle part and a lattice bony septum, and a lattice bony septum. In the lead storage battery equipped with the pole pillar or bonding object drawn from the shelf which carries out the cluster weld of the polar plate handle part of this polarity, and this shelf The positive electrode member which consists of a positive electrode lattice, a positive electrode shelf, a positive electrode pole pillar, and a positive electrode bonding object consists of lead or the lead alloy which does not contain the substance top Sb. The part except a negative electrode lattice bony septum consists of lead or the lead alloy which does not contain the substance top Sb among the negative electrode members which consist of a negative electrode lattice, a negative electrode shelf, a negative electrode pole pillar, and a negative electrode bonding object. Either a negative electrode lattice bony septum or negative electrode active material is the lead storage battery characterized by the content to said amount of negative electrode active material of Sb being 0.001 to 0.1 mass % including Sb.

[Claim 2] The lead storage battery according to claim 1 which carries out that the content to this negative electrode active material of Sb is 0.001 mass % - 0.02 mass % to negative electrode active material with the feature including Sb.

[Claim 3] The lead storage battery according to claim 1 to 2 characterized by having the lead alloy layer of the surface which touches the positive active material of said positive electrode lattice for which Sn is contained 2% or more in part at least.

[Detailed Description of the Invention]**[0001]**

[Field of the Invention] Especially this invention relates to the lead storage battery which does not contain antimony (Sb) in the member which constitutes a positive electrode.

[0002]

[Description of the Prior Art] Although the Pb-Sb alloy was used for the positive electrode lattice body of the conventional lead storage battery, there was a problem that **** was not mostly excellent in preservation characteristics etc. As this Reason, when the charge and discharge of the lead storage battery are carried out, it is because Sb gradually contained in the positive electrode lattice body is eluted, the hydrogen overvoltage in a negative electrode falls by Sb which deposited and deposited to the negative electrode and it becomes easy to generate hydrogen gas. If the charge and discharge of a cell are furthermore performed continuously then, Sb precipitation amount on a negative electrode will increase, and **** will advance further. Even if **** advances, when water refilling is neglected, a negative electrode shelf and a negative electrode handle part are exposed from an electrolyte. Once these negative electrode members were exposed from the electrolyte, corrosion advanced rapidly, and there was a problem which results in a short life.

[0003]

[Problem to be solved by the invention] In order to control a short life by such corrosion and this in recent years, to the positive electrode lattice body, the cell with the outstanding maintenance-free nature using the Pb-Ca-Sn alloy which does not include the substance top Sb has become common. However, generally using the Pb-Sb alloy containing Sb for the positive electrode column or positive electrode bonding object which drew the positive electrode plate from the positive electrode shelf which carries out a cluster weld, or the shelf has been performed.

[0004] Although low water loss falls substantially as compared with the storage battery by which the storage battery using Pb alloy which does not contain Sb in a positive electrode lattice body used the Pb-Sb alloy, it has turned out that there is an inclination in which Sb contained in the shelf, pole pillar, and bonding object of a positive electrode in the end of life of a storage battery carries out a segregation to the portion centering on a negative electrode handle part. When the negative electrode handle part in which such Sb carried out the segregation was exposed from an electrolyte, corrosion advanced on the surface of a negative electrode handle part and thickness became thin, the technical problem that the hardness of a handle part will fall occurred.

[0005]

[Means for solving problem] In order to solve the above mentioned technical problem, invention of Claim 1 of this invention has the positive electrode plate equipped with the positive electrode lattice which consists of a negative electrode plate and

a lattice handle part equipped with the negative electrode lattice which consists of a lattice handle part and a lattice bony septum, and a lattice bony septum. In the lead storage battery equipped with the pole pillar or bonding object drawn from the shelf which carries out the cluster weld of the polar plate handle part of this polarity, and this shelf The positive electrode member which consists of a positive electrode lattice, a positive electrode shelf, a positive electrode pole pillar, and a positive electrode bonding object consists of lead or the lead alloy which does not contain the substance top Sb. The part except a negative electrode lattice bony septum consists of lead or the lead alloy which does not contain the substance top Sb among the negative electrode members which consist of a negative electrode lattice, a negative electrode shelf, a negative electrode pole pillar, and a negative electrode bonding object. Either a negative electrode lattice bony septum or negative electrode active material is the lead storage battery characterized by the content to said amount of negative electrode active material of Sb being 0.001 to 0.1 mass % including Sb.

[0006] The lead storage battery characterized by the content to said amount of negative electrode active material of Sb being 0.001 to 0.1 mass % is shown including Sb.

[0007] Moreover, invention concerning Claim 2 of this invention shows the lead storage battery characterized by the content to this negative electrode active material of Sb being 0.001 mass % - 0.02 mass % to negative electrode active material in the lead storage battery of Claim 1 including Sb.

[0008] Furthermore, invention concerning Claim 3 of this invention shows at least the lead storage battery characterized by having the lead alloy layer of the surface which touches the positive active material of a positive electrode lattice in Claim 1 or the lead storage battery of 2 which contains Sn 2% or more in part.

[0009]

[Mode for carrying out the invention] The lead storage battery by the form of operation of this invention is explained using Drawings.

[0010] Drawing 1 is the **** figure showing the polar plate group 1 which constitutes the lead storage battery of this invention. The positive electrode plate (not shown) has the architecture with which the active material was filled up into the positive electrode lattice body which consists of a positive electrode handle part 1 and a positive electrode lattice bone (not shown). This positive electrode plate and the negative electrode plate 2 have countered mutually through a separator 3.

[0011] The negative electrode plate 2 has the negative electrode lattice body 6 which consists of a negative electrode handle part 5 and a negative electrode lattice bone 4. The cluster weld of the handle parts of this polarity is carried out, the positive electrode shelf 8 and the negative electrode shelf 7 are formed, respectively, and a pole pillar or a bonding object is formed in each shelf. the example shown in drawing 1 -- a positive electrode and a negative electrode -- each -- the example which established the positive electrode bonding object 8 and the negative electrode bonding object 9 is shown in the shelf.

[0012] In this invention, the positive electrode handle part 1, a positive electrode lattice bone, the positive electrode shelf 8, the positive electrode bonding object 8, and a positive electrode pole pillar (these are named generically and it is a positive electrode member) consist of Pb(s) or Pb alloys which do not include the substance top Sb. However, Sb contained as an about several ppm impurity removes. Since oxidation corrosion advances in a positive electrode, it is desirable to use a Pb-Sn alloy.

[0013] On the other hand about a negative electrode, the negative electrode handle part 5, the negative electrode shelf 7, the negative electrode bonding object 9, and a negative electrode pole pillar consist of Pb(s) or Pb alloys which do not include the substance top Sb like a positive electrode member. However, even if there is little negative electrode lattice body 6 or negative electrode active material, it constitutes so that Sb may be included in either. When making a negative electrode lattice body contain Sb, in constituting the negative electrode lattice body 6 from a Pb-Ca alloy especially in a maintenance-free cell, on the layer and concrete target which contain Sb on Pb-Ca alloy surface, it arranges a Pb-Sb alloy layer. In making Sb contain in negative electrode active material, it adds Sb to raw material lead powder of an active material.

[0014] The amount of Sb(s) added in this invention in the negative electrode lattice body 6 or negative electrode active material is limited to the range of 0.001 mass % - 0.1 mass % to the amount of negative electrode active material. using such a polar plate group -- a law -- the lead storage battery of this invention can be obtained by assembling according to a method.

[0015] Moreover, when adding Sb especially to negative electrode active material, the addition of 0.001 - 0.02 mass % is desirable to the amount of negative electrode active material. Furthermore, it is desirable to arrange the Pb-Sn alloy layer of the surface which contacts the positive active material of a positive electrode lattice body preferably which contains Sn more than 2 mass % in part at least.

[0016] The cell by the architecture of this this invention controls growth in **** at the time of the life cycle which is the technical problem mentioned above, and cancels the corrosion in a negative electrode, and contributes the outstanding life engine performance.

[0017]

[Working example] The cell by the example of this invention and the conventional example was created, and assessment of the existence of the corrosion of low water loss and a negative electrode handle part and charge acceptance nature was performed by doing an overcharge check and an overdischarge check.

[0018] Alloy composition is Pb-0.07 mass %Ca-1.3 mass %Sn, using a Pb-Ca-Sn alloy in the positive electrode lattice body of the lead storage battery of this invention. After rolling this alloy (sheet 1) gradually, expanded processing was performed and the lattice body was formed, and it was filled up with the active material paste, and the positive electrode plate (P1) was produced. Moreover, the Pb-7 mass %Sn alloy (sheet 2) about 0.2mm thick was laid on top of the sheet 1, it rolled gradually, and the positive electrode plate (P2) was produced through the same process as henceforth. On the other hand, the negative electrode plate created the lattice body through expanded processing, after rolling the Pb-0.07 mass %Ca-0.25 mass %Sn

alloy (sheet 3) like the positive electrode. Then, the lattice body was filled up with the active material paste which did 0.010 mass % addition of Sb to the amount of active materials, and the negative electrode plate (N1) was obtained. Moreover, the Pb-2 mass %Sb alloy (sheet 4) about 0.2mm thick was laid on top of the sheet 4, it rolled gradually, and the negative electrode plate (N2) was produced through the same process as henceforth. In the separator, the bag-like separator of the form where a positive electrode plate is wrapped in was produced using the sheet made from microporous polyethylene about 0.3mm thick.

[0019] The lead storage battery for automobiles of 55D23 type (12V48Ah) was produced using the polar plate group which consists of five positive electrode plates per one cell, and six negative electrode plates using two kinds of above-mentioned positive electrode plates, and two kinds of negative electrode plates. Moreover, when forming plates very much, it was made the bonding object which joins between the shelf which connects the polar plate in a positive electrode, and a cell with the architecture which does not contain Sb in the whole positive electrode using the alloy which does not contain Sb.

[0020] Moreover, it piled up (it is based on the conventional manufacturing method) for the comparison, the Pb-7 mass %Sb alloy (sheet 5) about 0.2mm thick was laid on top of the sheet 1, it rolled gradually, and the positive electrode plate was produced through the same process as henceforth (P0). The negative electrode plate rolled the sheet 3 gradually, and produced it through the same process (N0). The cell of the architecture using this lattice body was used as the cell of the conventional example. The conditions of detailed cell architecture are shown in Table 1.

[0021]

[Table 1]

	電池 No.	電池構成			①過充電試験		②過放電放電試験
		正極の極・極板形状	正極格子体との表面層	負極内のSb	減重量	負極容量の(初期に 対する百分率)	充電受入性
従来例	A	Sb含有	Pb-Sb合金(P0)	なし(N0)	100%	82%	100%
本発明例	B1	Sbなし	なし(P1)	正極面に含有(N1)	78%	90%	92%
	B2	Sbなし	なし(P1)	格子体上の 裏面層に含有(N2)	79%	98%	43%
	C1	Sbなし	Pb-Sb合金(P2)	正極面に含有(N1)	79%	98%	98%
	C2	Sbなし	Pb-Sb合金(P2)	格子体上の 裏面層に含有(N2)	88%	98%	102%

[0022] << check 1>> -- in order to evaluate the corrosion in the low water consumption and the negative electrode which are a technical problem about the cell of architecture of differing respectively, life test of the following antenna radiation patterns was carried out. This life test is a test pattern supposing how an overcharge inclination is used, and repeated the cycle which performs 13.8V constant potential charge continuously in the 75-degree-C atmosphere for 120 hours. Moreover, in order to assume the condition that **** advanced and the polar plate upper part was exposed from the electrolyte, where an electrolyte is reduced to the lower limit level, it examined. Then, clearance and measurement of negative electrode lug thickness were performed for the corrosion product generated on the negative electrode lug surface, and it asked for the ratio of the lug thickness after the termination of test to the lug thickness of an initial state by the percentage.

[0023] This test result is shown in Table 1. The life test assessment in a table compared the cell which sets to 100 the low water loss and the corrosion rate of Cell A which consist of the conventional architecture, and consists of each architecture. It is the architecture which the cell A of the conventional example contains Sb on the bonding object of a part as shown in drawing 1 in a positive electrode, a shelf, and the lattice body surface, and does not contain Sb in a negative electrode. On the other hand, the cells B1-C2 of this invention are cells of architecture of that each cell contains Sb in a negative electrode in a positive electrode excluding Sb. It was a result with as little [for the examples B1-C2 of this invention] low water loss to the conventional example A as [about about 70 to 80 percent]. Although especially the conventional example A had little **** in the first stage, when the cycle advanced, the inclination for **** to increase gradually was seen. Sb contained in the positive electrode is eluted and this deposits to a negative electrode as a cycle advances, and it is considered to originate in hydrogen overvoltage falling and hydrogen gas being generated. Although there are also few Sb precipitation amounts from a positive electrode to a negative electrode the first stage, it is thought that Sb precipitation amount also increased gradually with cycle progress, and **** increased. On the other hand, this inventions B1-C2 are eliminating Sb of a positive electrode and giving very small quantity Sb beforehand to a negative electrode, and can be assumed to be the results which canceled buildup of **** accompanying cycle progress and have been controlled to moderate low water loss. Moreover, in B1 and B-2, there was slightly much low water loss of B1. Although this Reason is not clear, since Sb exists on negative electrode active material, B1 can consider that the reaction surface area on Sb is wide range than B-2.

[0024] Moreover, in B1-C2 which are an example of this invention, corrosion was not seen at all, but the conventional example A was in the same condition as the first stage, although progress of corrosion was seen in the negative electrode shelf and the handle part. It can be guessed that Sb contained in the positive electrode of the conventional example A originates as this Reason. As mentioned above, although Sb of a positive electrode is eluted with cycle progress and deposits to a negative electrode, it deposits in the upper part considered that reaction availability is high also within a polar plate mostly. It is presumed that Sb carries out a segregation to the shelf, polar plate handle part, and cope box bone which are not covered in particular with an active material (the handle part and cope box bone of a negative electrode plate are shown in drawing 2). According to cycle progress, the part in which Sb carried out the segregation is exposed, and the

surface is considered that it is covered with thin liquid membrane and pH increases. Then, the dissolution of Pb takes place easily according to pH buildup, on Sb, hydrogen gas is generated, the local cell which Pb dissolves on Pb and lead sulfate generates is formed, and it is guessed that corrosion is advancing. On the other hand, without being eluted to an electrolyte and depositing in the negative electrode upper part, since the examples B1-C2 of this invention do not contain Sb in a positive electrode, even if electrolytes decrease in number and the negative electrode upper part is exposed, in order not to form a local cell, it is thought that corrosion did not advance, and it can be said that corrosion is prevented. Moreover, the difference was not looked at by corrosion in the examples B1-C2 of this invention. It can say that it is because Sb of the positive electrode was eluted also from this as for corrosion and it has deposited to the negative electrode upper part, and it is thought by the cell which Sb does not contain in a positive electrode that a difference was not seen.

[0025] The check which assumed overdischarge neglect apart from << check 2>>, next life test supposing the above mentioned overcharge inclination was done. After this test condition carried out constant current discharge by 9.6A for 5 hours, it connected the load of 10W in the 40-degree-C atmosphere, discharged it for 14 days, removed load, changed it into the open circuit condition, and was succeedingly neglected for 14 days in the 40-degree-C atmosphere. Then, after carrying out recovery charge by 15.0V for 4 hours, 5 hour-rate discharge estimated capacity. This test result is shown in (Table 1). The test assessment in a table compared the cell which sets to 100 recovery capacity of the conventional example A which consists of the conventional architecture, and consists of each architecture. As compared with the conventional example A, the example B1 of this invention and B-2 are remarkable, and capacity was falling. By the way, the effect which eases the effect of the non-**** film which Sb layer of the positive electrode lattice surface of the conventional example A generates to the interface of a lattice body and an active material after overdischarge neglect with the effect of raising the charge acceptance nature described previously is known. Therefore, B1 and B-2 are considered that capacity fell without being unrecoverable even if it is influenced by the nonconducting film of the interface generated by overdischarge neglect and charges. On the other hand, capacity with the examples C1 and C2 of this invention equivalent to the conventional example A was obtained. This can presume being able to consider the effect as Sb layer of the conventional example A that the Sn layer of the positive electrode lattice body surface in the examples C1 and C2 of this invention is the same, and easing the effect of the nonconducting film of the generated interface.

[0026] As mentioned above, do not contain Sb in a positive electrode but a negative electrode is set to the part except the bonding object which connects between cells, the shelf which welds a polar plate, and a polar plate handle part. To the amount of negative electrode active material, the lead storage battery of architecture of carrying out controls growth in **** at the time of the life cycle which is a technical problem, and cancels the corrosion in a negative electrode, and 0.001 mass %-0.1 mass % inclusion contributes the outstanding life engine performance for Sb. Moreover, the lead storage battery of the above-mentioned architecture using the positive electrode plate which assumes also in overdischarge neglect and forms the lead alloy layer of the positive electrode lattice body surface for which more than 2 mass % contains Sn in part at least is desirable.

[0027]

[Effect of the Invention] As mentioned above, the lead storage battery of architecture of not containing Sb in a positive electrode but containing Sb in very small quantities to the amount of negative electrode active material in a negative electrode can have the life characteristic which controlled growth in **** at the time of a life cycle, and maintained moderate low water loss, and canceled the corrosion in a negative electrode, and was excellent. Also when overdischarge is carried out, especially as for the lead storage battery of the above-mentioned architecture using the positive electrode plate which forms the lead alloy layer of the positive electrode lattice body surface for which more than 2 mass % contains Sn in part at least, the characteristics which prevented capacity lowering and were stabilized can be obtained.

[Translation done.]

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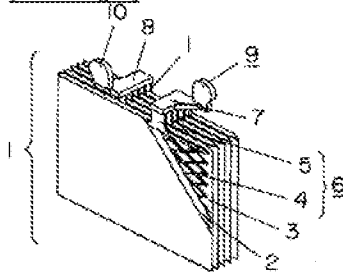
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DRAWINGS

[Drawing 1]



[Translation done.]